

incorporate the following features (17):

1) Measurements should be made throughout the entire atmosphere, including the highest cloud and haze layers. Entry probes should begin measuring the solar flux at as high an altitude as practical, and there should be complementary optical measurements from an orbiting spacecraft to obtain the atmospheric reflectivity and the scattering properties of the cloud top region.

2) Both the downward flux and the upward flux should be measured with entry probes. This provides a direct measurement of the vertical distribution of absorbed energy, and it allows a model-independent determination of the ground albedo.

3) Both narrow-band and broad-band measurements should be made. The cloud layering can best be obtained from narrow-band measurements, while the vertical distribution of absorbed solar energy requires integration over the entire solar spectrum (18).

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6. The photometer measured the quantity

$$W = \int_0^2 S(\lambda) d\lambda 2\pi \int_0^{\pi/2} I(\lambda, \phi) P(\phi) \sin\phi d\phi$$

where $I(\lambda, \phi)$ is the intensity of radiation (watt $m^{-2} \mu m^{-1} \text{ster}^{-1}$) of wavelength λ at the angle ϕ from the vertical axis of the photometer, $S(\lambda)$ is the spectral sensitivity of the photometer, and $P(\phi)$ is its angular sensitivity; $P(\phi)$ was such that W is essentially the downward flux (1, 2).

7. This flux includes the spectral sensitivity of the photometer. The uncertainty in the flux above the atmosphere arises primarily from the uncertainty in the location of the Venera 8 landing, which was such that the solar elevation above the horizon was $5.5^\circ \pm 2.5^\circ$. V. S. Avdukevsky *et al.* (2) give the value 65 watt/ m^2 for the flux just above the atmosphere. We obtain 55.5 watt/ m^2 by using the spectral sensitivity in figure 1 of Avdukevsky *et al.* and the solar flux of M. P. Thekaekara [*Sol. Energy* **14**, 109 (1973)].
8. The cloud top level, defined as the level where the cloud optical depth is unity, is at the pressure 50 ± 25 mbar (9). At the first Venera 8 data point (altitude 48.5 km) the temperature and pressure were measured as $329^\circ K$

and 1.09 bars. The pressure 50 mbar corresponds to altitude ~ 68 km [see G. Fjeldbo, A. J. Kliore, V. R. Eshleman, *Astron. J.* **76**, 123 (1971)].

9. J. E. Hansen and J. W. Hovenier, *J. Atmos. Sci.* **31**, 1137 (1974).
10. The multiple scattering method which we use is described in A. A. Lacis and J. E. Hansen, *J. Atmos. Sci.* **31**, 118 (1974). At each wavelength the doubling method is applied to obtain the reflection and transmission for each homogeneous layer; the layers are combined by using the adding method to obtain the reflection and transmission from the complete inhomogeneous atmosphere and the vertical distribution of absorbed radiation; finally, the results are weighted by the solar flux and the photometer's spectral and angular response and integrated over wavelength to obtain the transmission which would be measured as a function of altitude.
11. The Rayleigh optical thickness above pressure P is

$$\tau^R = \frac{P}{g\bar{\mu}} \left[\frac{8\pi^3}{3\lambda^4 N^2} \sum_i v_i (n_i^2 - 1)^2 \frac{6 + 3\delta_i}{6 - 7\delta_i} \right]$$

where g is the acceleration of gravity, $\bar{\mu}$ is the mean molecular mass, N is the number density of molecules, v_i is the fraction by volume of gas i , n_i is the refractive index of gas i , and δ_i is the depolarization factor of gas i (see J. E. Hansen and L. Travis, *Space Sci. Rev.*, in press); Loschmidt's number may be used for N if the other quantities in the square brackets are evaluated at standard temperature and pressure.

12. This is an adequate approximation for particles which are larger than the wavelength and have little absorption. Polarization measurements show that the particles in the visible clouds have a radius of about $1 \mu m$ (9). Photometric observations show that the spherical albedo is high, of the order of 80 to 90 percent, for the wavelength region 0.5 to $0.8 \mu m$ [see W. M. Irvine, *J. Atmos. Sci.* **25**, 610 (1968)].
13. The similarity relations are discussed, for example, by H. C. van de Hulst and K. Grossman [in *The Atmospheres of Venus and Mars*,

J. C. Brandt and M. B. McElroy, Eds. (Gordon & Breach, New York, 1968), p. 35] and J. E. Hansen [*Astrophys. J.* **158**, 337 (1969)]. We have verified that the similarity relations are accurate for the present problem by making computations with a number of different phase functions.

14. If τ^R is the Rayleigh optical depth due to scattering by air molecules and τ^c the optical depth due to cloud particles (including any aerosols or haze), then turbidity $\equiv d\tau^c/d\tau^R$. A numerical value can be assigned to the turbidity by choosing a reference wavelength.
15. The phase function was obtained from Mie scattering theory at $\lambda = 0.65 \mu m$ for refractive index 1.44 and size distribution $n(r) \propto r^{(1-3b)/b} e^{-r/a}$ where r is the radius, $a = 1.05 \mu m$ and $b = 0.07$ (9). For anisotropic scattering τ^c and $\tilde{\omega}^c$ in Fig. 2 refer to the scaled quantities, $\tau^c(1 - \langle \cos\alpha \rangle)$ and $1 - (1 - \tilde{\omega}^c)/(1 - \langle \cos\alpha \rangle)$, where the asymmetry parameter $\langle \cos\alpha \rangle$ is 0.686.
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17. To some extent these recommendations are included in the plans for Pioneer Venus ("Pioneer Venus multiprobe mission preliminary scientific payload," Ames Research Center, Moffett Field, California, 1973). Radiometers on the entry probes will measure both upward and downward radiation. The entry probe measurements may begin as high as the 50-mbar level; this is higher than the level of the first Venera 8 measurements (~ 1 bar), but beneath a significant optical thickness of cloud and haze particles. No narrow-band measurements are planned for the entry probes. The instruments for the orbiting spacecraft had not been selected at the time of this writing.
18. The spectral region of the photometer on Venera 8, ~ 0.5 to $0.8 \mu m$, contains only about 33 percent of the solar flux. The spectral albedo of Venus [see figure 2 in G. P. Kuiper, *Commun. Lunar Planet. Lab.* **101**, 1 (1969)] is such that the interval 0.5 to $0.8 \mu m$ contains only about 10 percent of the solar flux absorbed by Venus. Thus, even if accurate and complete data were obtained for that region, only a small part of the solar energy input would be defined.

1 March 1974

Carbonate Compensation Depth: Relation to Carbonate Solubility in Ocean Waters

Abstract. *In situ calcium carbonate saturation measurements suggest that the intermediate water masses of the central Pacific Ocean are close to saturation with respect to both calcite and local carbonate sediment. The carbonate compensation depth, located at about 3700 meters in this area, appears to represent a depth above which waters are essentially saturated with respect to calcite and below which waters deviate toward undersaturation with respect to calcite.*

The variability of carbonate content in marine sediments was first observed almost a century ago by Murray and Renard (1), who reported the lack of carbonate-rich sediments in the deepest part of the oceans. Studies in subsequent years (2) have confirmed the observation of the *Challenger* expedition and showed that the transition zone between carbonate-rich and carbonate-poor sediments may be sharp. As the source of most carbonate material is at the ocean surface (tests and skeletons of marine plankton) and as its removal at depth is due to dissolution, this transition zone defines a horizon where the carbonate supply is compensated by the rate of dissolution. The depth of this boundary,

usually referred to as the carbonate compensation depth, is not constant in the oceans as, by definition, it is related to surface productivity and the chemistry of deep ocean waters—both of which are variable. Investigation of the factors controlling calcium carbonate dissolution in the oceans is essential because carbonate deposition on the ocean floor is a major sink of carbon and hence an important factor in the mass balance of carbon on the earth.

The carbonate compensation depth was originally explained as the boundary line between supersaturated and undersaturated ocean waters (1). It was argued that below the compensation depth, seawater is undersaturated with

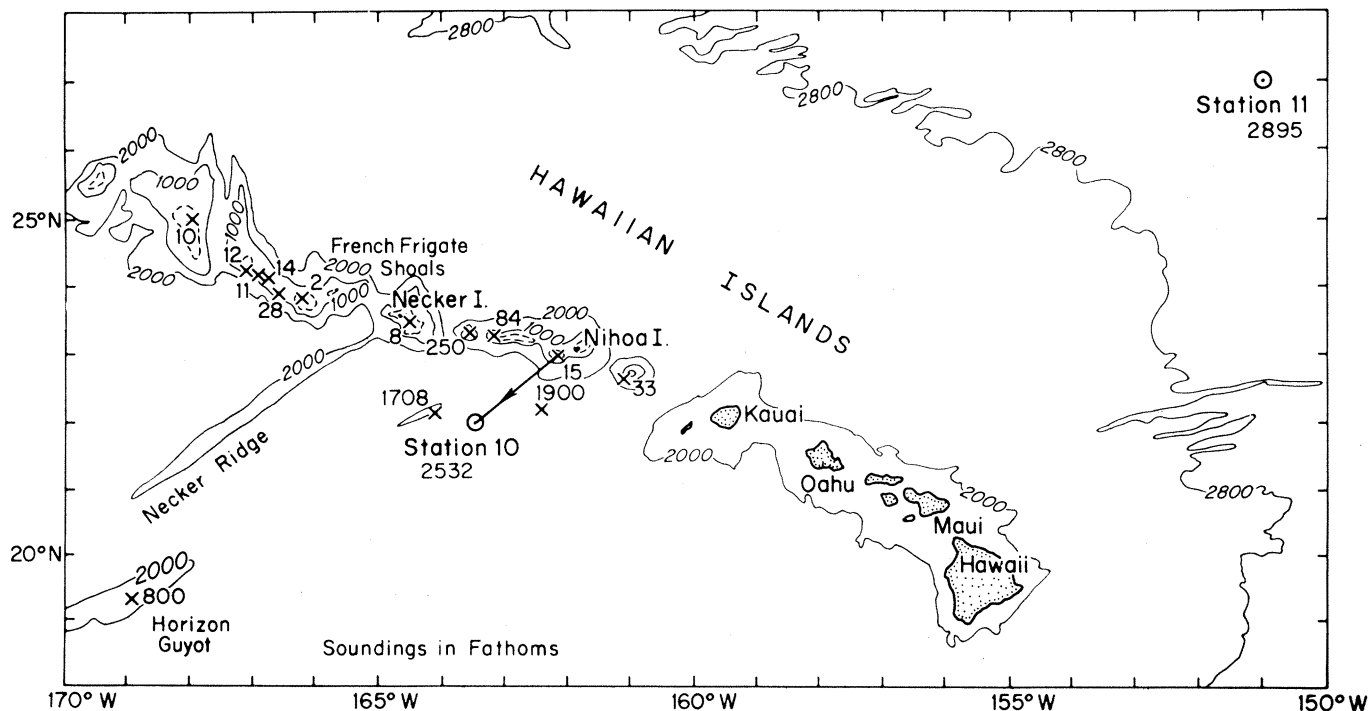


Fig. 1. Map of the study area. The maximum water depths are 4700 m in station 10 and 5300 m in station 11 (1 fathom $\approx$ 1.8 m). Sediments were sampled along the slope marked by an arrow pointing to station 10. Topographical details irrelevant to this report have been omitted from the map.

respect to calcite (the least soluble form of CaCO_3) and all carbonate material reaching these waters dissolves. However, recent estimates (3) of carbonate saturation in the oceans, derived from laboratory analyses of sampled waters at atmospheric pressure, suggest that the carbonate saturation depth is much shallower than the carbonate compensation depth. These estimates, which assume precise knowledge of many thermodynamic constants at the in situ conditions, conflict with direct satumeter measurements previously reported (4). Here we present new data, which relate carbonate saturation in the water column to the carbonate compensation depth in the central Pacific Ocean.

The study was conducted in two adjacent areas (Fig. 1), one south of the Hawaiian Islands chain and the other about 1300 km northeast of the islands. Bottom depths were measured as 4700 m (station 10) and 5300 m (station 11). The carbonate compensation depth was investigated by sampling the sediment surface along a slope (marked as an arrow pointing to station 10 in Fig. 1), and later analyzing for CaCO_3 content. The latter was determined by weighing dry, washed sediment samples before and after treatment with 1N HCl.

Direct determinations of CaCO_3 solubility in central Pacific waters were con-

ducted with an in situ carbonate satumeter developed in our laboratory (5). Measurements were made by exposing different CaCO_3 minerals to ambient seawater at depth and monitoring the pH shifts due to the chemical reaction. This information, along with other parameters of the waters, was then used to calculate the degree of satura-

tion (6), defined as the ratio $IP/K'sp$ —where IP is the product of the concentrations of total dissolved calcium (Ca^{2+}) and carbonate (CO_3^{2-}) ions and $K'sp$ is the apparent solubility product of the carbonate mineral (7)—at the depth of measurement (8). The satumeter experiments reported here were conducted with three CaCO_3 forms:

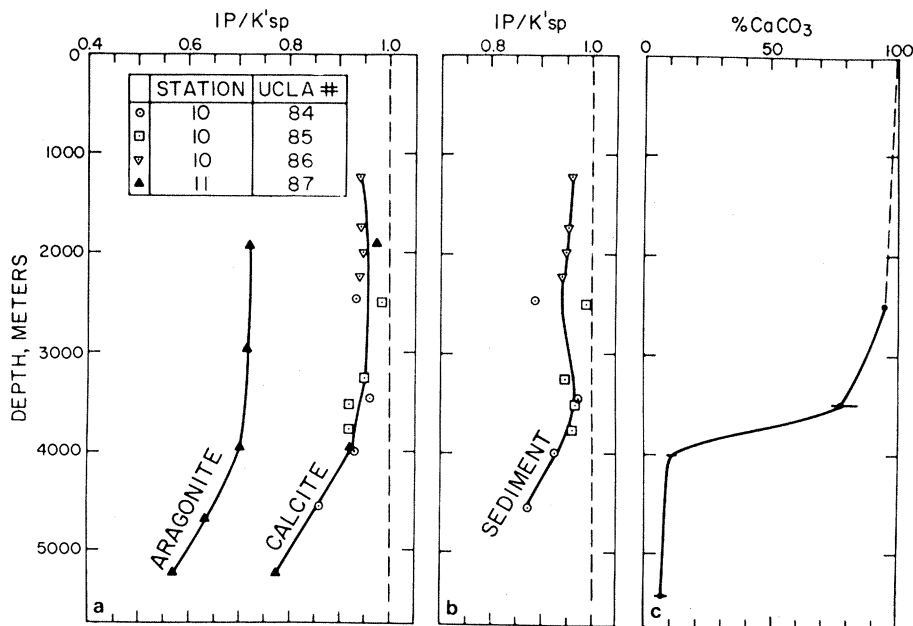


Fig. 2. Profiles of the degree of saturation of seawater with respect to (a) standard calcite and aragonite and (b) local sediment (all separated by sieving to the size range 0.35 to 0.50 mm) compared to (c) the carbonate content in adjacent sediment. The degree of saturation is given by $IP/K'sp$ (see text for definition).

standard calcite, aragonite (9), and carbonate sediments sampled from the slope adjacent to station 10 (Fig. 1). The sediments were raised from a depth of 2000 m and sieved to the size range 32 to 42 mesh (0.35 to 0.50 mm) before use in the saturometer cell. X-ray diffraction analyses revealed no traces of aragonite in the calcite standard, whereas calcite traces were present in the standard aragonite. The sediment separate used in experiments was found to be pure calcite; however, traces of aragonite were found in the finest fraction of the sediment.

The data (Fig. 2) show a correlation between the degree of carbonate saturation of seawater and the carbonate content of the sediments at the same depth. The results of the in situ carbonate measurements suggest that the intermediate waters of the central Pacific, between approximately 1000 and 3500 m, are close to saturation ($IP/K'sp \approx 0.95$) with respect to calcite (10). At about 3750 m, the degree of saturation profile exhibits a break and deviates toward undersaturation. Measurement of seawater saturation with respect to the local sediments duplicates that with respect to standard optical calcite, except that deviation toward undersaturation seems to start at a somewhat shallower depth. However, the significance of this difference cannot be assessed because of the scatter in the data and the small number of replicate measurements.

The profile of seawater saturation with respect to aragonite parallels that with respect to calcite, but is shifted toward undersaturation, because aragonite is more soluble than calcite (7). Hence, there is good consistency between the experiments conducted with calcite, aragonite, and local sediments. Further, the data from station 11 correlate well with the data from station 10, which suggests similar carbonate solubility reactions along the two profiles.

The data reported here reveal that the zone between high and low carbonate content in the sediments coincides with the break in the calcite-seawater saturation profile (Fig. 2). This observation is in accord with data on carbonate dissolution rates in the central Pacific obtained by measuring the weight loss of carbonate material suspended for several months on mooring lines (11). Dissolution rates of both optical grade calcite and foraminiferal ooze were found to increase rapidly below approximately 3700 m.

Conceivably, the carbonate compensation depth may be depressed with respect to the break in the calcite saturation profile in areas with high productivity, that is, a high sedimentation rate of biogenic CaCO_3 . We believe that further studies are essential before this can be proved.

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8. The ratio $IP/K'sp = 1$ signifies saturation with respect to the carbonate minerals, whereas ratios smaller or larger than unity signify undersaturation or supersaturation, respectively.
9. Materials were obtained from Ward's (Monterey, California). The calcite was an optical grade mineral from Chihuahua, Mexico, and the aragonite was from Farka, Switzerland. The minerals were crushed, sieved to the size range 32 to 42 mesh (0.35 to 0.50 mm), washed, and then dried overnight in an oven at 105°C.
10. Laboratory experiments seem to indicate that the slight undersaturation observed may be due to the presence of traces of a high-solubility phase in the carbonate material used, and does not represent the characteristics of the bulk solid.
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12. We thank P. Greene and D. Friedman for assistance in constructing and testing the instrumentation used in this study, D. Winter for analyzing sediments, and Scripps Institution of Oceanography for making the R.V. *Alexander Agassiz* available to us. The National Science Foundation is gratefully acknowledged for supporting this research (grant GA-34104).

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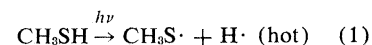
Hot Hydrogen Atoms: Initiators of Reactions of Interest in Interstellar Chemistry and Evolution

Abstract. Photochemically generated hot hydrogen atoms initiate reactions with simple molecular substrates including methane to produce organic alcohols, amines, acids, amino acids, and other compounds. The typical quantum yields for the formation of amino acids are 2×10^{-5} to 4×10^{-5} . Hot hydrogen atoms may be important initiators of reactions in interstellar space and in planetary atmospheres.

Considerable effort has been made to elucidate the pathways by which biologically significant molecules arose prior to the existence of living things (1). Many of the techniques consisted of conventional electric discharge and ultraviolet irradiation or the heating of mixtures of various simple molecules such as NH_3 , CH_4 , and water. In most cases, prime areas of interest included the chemical synthesis of amino acids, purines, and pyrimidines, and ultimately polypeptides and polynucleotides. In a more recent effort, H_2S irradiated in the presence of a mixture of simple gases yielded certain amino acids (2). In addition, there is considerable interest in the mechanism of formation of molecules in interstellar space. We report here the formation of some amino acids and other organic compounds initiated by "hot" hydrogen atoms in mixtures of simple gases chosen from among CH_4 , C_2H_6 , H_2O , and

NH_3 . The hot hydrogen atom donors include both H_2S and CH_3SH .

Hot hydrogen atoms are those with kinetic (or translational) energy in excess of that to be expected if they were in thermal equilibrium with the surroundings. In our case, they are generated by photolysis of the donor molecules as



The excess kinetic energy of hydrogen from HR is

$$E_k(\text{H}) = (h\nu - D - I) \frac{M_R}{M_{\text{HR}}} \quad (2)$$

where $h\nu$ is the energy of light, D is the bond dissociation energy, I is the internal energy remaining in the fragment R, and M is the mass. For the donors used, the mass ratio is essentially equal to 1 and the amount of internal energy left in R is approximately 5 to 17 percent of the maximum kinetic